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FORM PTO-1390 (REV 10-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: P/167-133

U.S. APPLICATION NO. (If known, see 37 CFR 1.5): 09/807457

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP98/06558	15 October 1998	

TITLE OF INVENTION: MOULDED BODIES MADE FROM A POLYURETHANE MATERIAL, PRODUCTION AND USE THEREOF

APPLICANT(S) FOR DO/EO/US: Thomas BUCHEL

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
4. ☐ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). **(unsigned)**
10. ☒ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). (Amended claims)

Items 11 to 16 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
    pefs print form.

EXPRESS MAIL CERTIFICATE

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail Post Office to Addresses (mail label EL613112700US in an envelope addressed to: Asst. Commissioner for Patents, Washington, D.C. 20231, on April 12, 2001.

Dorothy Jenkins
Name of Person Mailing Correspondence

Dorothy Jenkins
Signature

April 12, 2001
Date of Signature

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/807457	PCT/EP98/06558	P/167-133

17. [X] The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

	CALCULATIONS	PTO USE ONLY
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1000.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	24 - 20 =	4	X $18.00	$ 72.00	
Independent claims	3 - 3 =	0	X $80.00	$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $270.00	$	

TOTAL OF ABOVE CALCULATIONS =	$ 932.00	
[X] Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.	$	
SUBTOTAL =	$ 466.00	
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +	$	
TOTAL NATIONAL FEE =	$ 466.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +	$	
TOTAL FEES ENCLOSED =	$ 466.00	
	Amount to be refunded:	$
	charged:	$

a. [X] A check in the amount of $ 466. to cover the above fees is enclosed. **Check No.** 4207

b. [ ] Please charge my Deposit Account No. ________ in the amount of $________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0700. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

OSTROLENK, FABER, GERB & SOFFEN, LLP
1180 Avenue of the Americas
New York, NY 10036-8403

Tel: (212) 382 0700

SIGNATURE:

William O. Gray, III
NAME

30,944
REGISTRATION NUMBER

P/167-133

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Thomas BÜCHEL

Date: April 12, 2001

Serial No.:

Group Art Unit:

Filed:

Examiner:

For: MOULDED BODIES MADE FROM A POLYURETHANE MATERIAL, PRODUCTION AND USE THEREOF

Asst. Commissioner for Patents

Washington, D.C. 20231

AMENDMENT/SUBMISSION

Prior to examination, please amend the application as follows.

FEE CALCULATION

Any additional fee required has been calculated as follows:

_____ If checked, "Small Entity" status is claimed.

	NO. CLAIMS AFTER AMENDMENT		HIGHEST NO. PREVIOUSLY PAID FOR		EXTRA PRESENT		RATE	ADDIT. FEE
TOTAL	24	MINUS	20	* =	4	X	($9 SE or $18)	$ 72.00
INDEP.	3	MINUS	3	** =	0	X	($40 SE or $80)	$
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM						X	($135 SE or $270)	$
* not less than 20 ** not less than 3							TOTAL	$ 72.00

If any additional payment is required, a check which includes the calculated fee of $72.00 (OFGS Check No. ______) is attached.

In the event the actual fee is greater than the payment submitted or is inadvertently not enclosed or if any additional fee during the prosecution of this application is not paid, the Patent Office is authorized to charge the underpayment to Deposit Account No. 15-0700.

CONTINGENT EXTENSION REQUEST

If this communication is filed after the shortened statutory time period had elapsed and no separate Petition is enclosed, the Commissioner of Patents and Trademarks is petitioned, under 37 C.F.R. §1.136(a), to extend the time for filing a response to the outstanding Office Action by the number of months which will avoid abandonment under 37 C.F.R. §1.135. The fee under 37 C.F.R. § 1.17 should be charged to our Deposit Account No. 15-0700.

AMENDMENTS

_X_ If checked, amendment(s) to the specification and/or claims are submitted herewith.

1. ___ If checked, an abstract is submitted as the last page of Appendix A.

3. Claims:

Please amend claims 3-8, 10, 11, 16-19 and 22-24 pursuant to 37 C.F.R. § 1.121(c)(i) as set forth in the "clean" version attached hereto as Appendix A. Entry is respectfully requested. A version with markings to show the changes made pursuant to 37 C.F.R. § 1.121(c)(ii) is attached hereto as Appendix B.

___ If checked, the optional complete set of "clean" claims pursuant to 37 C.F.R. § 1.121(c)(3) is attached hereto as Appendix C.

REMARKS/ARGUMENT

This Preliminary Amendment is submitted to change the multiple dependent claims to single dependent claims in order to reduce the government filing fee.

EXPRESS MAIL CERTIFICATE

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail to Addressee (mail label # EL613112700US) in an envelope addressed to: Asst. Commissioner for Patents, Washington, D.C. 20231, on April 12, 2001:

Dorothy Jenkins
Name of Person Mailing Correspondence

Dorothy Jenkins
Signature

April 12, 2001
Date of Signature

Respectfully submitted,

William O. Gray, III
Registration No.: 30,944
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APPENDIX A

"CLEAN" VERSION OF EACH PARAGRAPH/SECTION/CLAIM
37 C.F.R. § 1.121(b)(ii) AND (c)(i)

CLAIMS (with indication of amended or new):

(Amended) 3. Method according to claim 1, characterised in that the curing by radical-triggered polymerisation occurs essentially without emissions.

(Amended) 4. Method according to claim 1, characterised in that the preform is produced in the shape of a film, tape, ribbon or any mould, and subsequently subjected to at least one further forming, preferably without the removal of material, for instance by bending, twisting, pressing, rolling, or deep-drawing.

(Amended) 5. Method according to claim 1, characterised in that to the starting components at least one of the following components is added: a filler, a fibre material, a coloured pigment.

(Amended) 6. Method according to claim 1, characterised in that a definite curing of the preform occurs by radical polymerisation of the free double bonds while applying elevated pressure and/or elevated temperature and/or irradiation with microwaves or energy-rich radiation, particularly ionising radiation.

(Amended) 7. Method according to claim 1, characterised in that to the mixture of starting components at least one catalyst adapted to trigger and/or accelerate a radical-type polymerisation of the reactive double bonds is added, particularly a hot-curing or photocatalyst, in an amount of up to 5 % by weight, preferably 0.1 to 1 % by weight.

(Amended) 8. Method according to claim 1, characterised in that two or more preforms, particularly in the form of films, tapes, ribbons, or plates, which are brought in mutual contact, preferably piled up as layers or glued together with the aid of an adhesion promoter, are bonded together while applying elevated pressure and elevated temperature to yield composites or laminates of any desired layer thickness, and definitely cured, where appropriate with the aid of light.

(Amended) 10. Method according to claim 5, characterised in that to the starting components a filler is added in a concentration of at most 80 % by weight, preferably of 20 to 75 and particularly of about 40 to 70 % by weight.

(Amended) 11. Method according to claim 5, characterised in that the fibre material is present in the form of unidirectional fibre strands, woven or nonwoven fibre fabric and preferably contains glass fibres, carbon fibres, aramide fibres, polyethylene fibres, cellulose fibres, and/or other suitable plastic fibres.

(Amended) 16. Moulded body according to claim 14, characterised in that it is colourless and translucent, more particularly crystal clear.

(Amended) 17. Moulded body according to claim 14, characterised in that it contains at least one of the following additives: filler, fibre material, coloured pigment, and/or exhibits a surface treatment, particularly a coating, coloration, painting and/or texture.

(Amended) 18. Moulded body according to claim 14, characterised in that it is present as a cured composite or laminate formed from at least two curable preforms.

(Amended) 19. Polyurethane-based moulded body that can be obtained by a method according to claim 1.

(Amended) 22. Use according to claim 20 for the production of technical formed parts, design and support elements, optical wave guides, tool components, covers and protective films, electrical, thermal or acoustic insulating elements, toys, utensils, art objects, or decorative objects.

(Amended) 23. Use of a moulded body according to claim 14 for the production of technical formed parts, design and support elements, optical wave guides, tool components, covers and protective films, electrical, thermal or acoustic insulating elements, toys, utensils, art objects, or decorative objects.

(Amended) 24. Use according to claim 20, for applications in medicine, dentistry, civil and mechanical engineering, fastening technology, insulating and packaging technology, the automotive industry, measuring technology, households, as well as in fine art.

APPENDIX B

VERSION WITH MARKINGS TO SHOW CHANGES MADE

37 C.F.R. § 1.121(b)(iii) AND (c)(ii)

CLAIMS:

3. Method according to [one of the claims 1 or 2] claim 1, characterised in that the curing by radical-triggered polymerisation occurs essentially without emissions.

4. Method according to [one of the claims 1 to 3] claim 1, characterised in that the preform is produced in the shape of a film, tape, ribbon or any mould, and subsequently subjected to at least one further forming, preferably without the removal of material, for instance by bending, twisting, pressing, rolling, or deep-drawing.

5. Method according to [one of the claims 1 to 4] claim 1, characterised in that to the starting components at least one of the following components is added: a filler, a fibre material, a coloured pigment.

6. Method according to [one of the claims 1 to 5] claim 1, characterised in that a definite curing of the preform occurs by radical polymerisation of the free double bonds while applying elevated pressure and/or elevated temperature and/or irradiation with microwaves or energy-rich radiation, particularly ionising radiation.

7. Method according to [one of the claims 1 to 6] claim 1, characterised in that to the mixture of starting components at least one catalyst adapted to trigger and/or accelerate a radical-type polymerisation of the reactive double bonds is added, particularly a hot-curing or photocatalyst, in an amount of up to 5 % by weight, preferably 0.1 to 1 % by weight.

8. Method according to [one of the claims 1 to 7] claim 1, characterised in that two or more preforms, particularly in the form of films, tapes, ribbons, or plates, which are brought in mutual contact, preferably piled up as layers or glued together with the aid of an adhesion promoter, are bonded together while applying elevated pressure and elevated temperature to yield composites or

laminates of any desired layer thickness, and definitely cured, where appropriate with the aid of light.

10. Method according to [one of the claims 5 to 9] claim 5, characterised in that to the starting components a filler is added in a concentration of at most 80 % by weight, preferably of 20 to 75 and particularly of about 40 to 70 % by weight.

11. Method according to [one of the claims 5 to 8] claim 5, characterised in that the fibre material is present in the form of unidirectional fibre strands, woven or nonwoven fibre fabric and preferably contains glass fibres, carbon fibres, aramide fibres, polyethylene fibres, cellulose fibres, and/or other suitable plastic fibres.

16. Moulded body according to [one of the claims 14 to 15] claim 14, characterised in that it is colourless and translucent, more particularly crystal clear.

17. Moulded body according to [one of the claims 14 to 16] claim 14, characterised in that it contains at least one of the following additives: filler, fibre material, coloured pigment, and/or exhibits a surface treatment, particularly a coating, coloration, painting and/or texture.

18. Moulded body according to [one of the claims 14 to 17] claim 14, characterised in that it is present as a cured composite or laminate formed from at least two curable preforms.

19. Polyurethane-based moulded body that can be obtained by a method according to [one of the claims 1 to 13] claim 1.

22. Use according to claim 20 [or 21] for the production of technical formed parts, design and support elements, optical wave guides, tool components, covers and protective films, electrical, thermal or acoustic insulating elements, toys, utensils, art objects, or decorative objects.

23. Use of a moulded body according to [one of the claims 14 to 19] claim 14 for the production of technical formed parts, design and support elements, optical wave guides, tool

components, covers and protective films, electrical, thermal or acoustic insulating elements, toys, utensils, art objects, or decorative objects.

24. Use according to [one of the claims 20 to 23] claim 20, for applications in medicine, dentistry, civil and mechanical engineering, fastening technology, insulating and packaging technology, the automotive industry, measuring technology, households, as well as in fine art.

MOULDED BODIES MADE FROM A POLYURETHANE MATERIAL, PRODUCTION AND USE THEREOF

TECHNICAL FIELD

The invention refers to a flexible, optionally elastic mouldable material on the basis of polyurethane (PU) that can be converted to a stable final form by subsequent curing, the material containing a polyurethane matrix having a plurality of reactive double bonds and particularly of ethylene-type unsaturated, radical-polymerisable groups present in a chemically bound form as part of the polyurethane matrix, for instance as an acrylic acid or acrylic acid derivative. The invention further relates to a process for producing cured moulded articles from this material and their use.

STATE OF THE ART

From the European patent document EP 0 262 488 the contents of which shall herewith be held to be included in the present specifications, a novel reactive organic filler in the form of a solid powder for polymerisable compositions is known which consists of a polyurethane material distinguished by a high content of reactive double bonds and which together with the components of the matrix to be filled, yields a durable compound between filler and matrix, particularly via copolymerisable groups. After complete polymerisation, products are thus obtained which have substantially improved crack resistance, strain resistance, and abrasion resistance. Such compositions have applications in diverse technical fields; they have attained particular significance as dental materials. The term of dental materials is understood to include dental fillings for conservative dental treatments and materials for the production of artificial teeth or parts of teeth such as crowns or inlays.

This polyurethane material which, in diverse modifications, is used as well in the present invention is generally crystal clear and is produced through a reaction not triggered by radicals. In addition it contains at least 0.5 mmole, preferably 0.5 to 5 and particularly 1.4 to 2.6 mmole of reactive double bonds per gramme of the poly-

urethane matrix (as determined by differential scanning calorimetry, DSC; details of this method are described in EP 0 262 488) which preferably are present as structural components of the polyurethane matrix and hence cannot be extracted with solvents.

In the following, the term "reactive double bonds" is to be understood primarily so as to include the double bonds that can be determined with the DSC method (see EP 0 262 488), unless another definition is specified in detail or another interpretation can be deduced from the context.

The high content of reactive double bonds that cannot be extracted is attained by polymerisation and cross linking of the starting components - preferably isocyanates as well as acrylates containing hydroxyl groups, particularly hydroxy(meth)acrylates - by a reaction not triggered by radicals, i.e., essentially by a polyaddition reaction (in the following also called the "urethane reaction"), so that 75 to 90 % of the ethylene-type unsaturated double bonds contained in the starting monomers are still present in the fully polymerised PU material. This feature allows the material to be subjected to a curing by radical-type polymerisation at any given time, for instance after intermediate storage.

The PU material which is employed as well for the purposes of the present invention is produced according to EP 0 262 488 by reacting (meth)acrylates containing hydroxyl groups with isocyanates while having a ratio of OH to NCO groups of approximately 1 : 1, and where at least one of the starting components is trifunctional or more highly polyfunctional in order to attain the degree of cross linking required for the different applications. According to a particularly favourable composition, a tri or polyisocyanate is used as the starting component, in which case the possibility arises to use less than the stoichiometric amount of hydroxy(meth)acrylate and achieve the required cross linking with water and/or a polyol, for instance an aliphatic triol, which react with the unreacted isocyanate groups forming urea or urethane groups. On the other hand one can also react a (meth)acrylate having three or more hydroxyl groups with a diisocyanate. Details of this way of preparation are known from EP 0 262 488.

Examples of suitable hydroxyl-functional (meth)acrylates are: bis(methacryloxy-2-hydroxypropyl) sebacate, bis(methacryloxy-2-hydroxypropyl) adipate, bis(methacryloxy-2-hydroxypropyl) succinate, bis-GMA (bisphenol A-glycidyl methacrylate), hydroxyethyl methacrylate (HEMA), polyethylene glycol methacrylate, 2-hydroxy and 2,3-dihydroxypropyl methacrylate, and pentaerythritol triacrylate.

Preferred isocyanates are aliphatic compounds such as 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, trimethylhexamethylene diisocyanate as well as the triisocyanate tris(6-isocyanatohexyl)biuret (Desmodur® N 100 of Bayer AG).

It is further known from EP 0 262 488 that the reaction between the hydroxy-(meth)acrylates and isocyanates can occur under mild conditions. The temperature is preferably about 10 to 60 °C. A catalyst can be added for acceleration; tertiary amines and organometal salts are suitable amongst others. Even the reaction of hydroxyl-functional (meth)acrylates is already known per se. It is employed for instance to produce prepolymers usable as binders in dental materials (cf. DE-OS 2 126 419).

According to EP 0 262 488, the PU material can also be produced by ionic copolymerisation of hydroxy(meth)acrylates with an epoxy resin and/or trioxane in stoichiometric ratios. For instance, bisphenol A-diglycidyl ether (Epikote® 828) can be reacted with glycidyl methacrylate and/or HEMA using BF_3 as a catalyst. Similar results are obtained when reacting glycidyl (meth)acrylate with trioxane or epoxides with epoxy(meth)acrylates. Further examples are the reaction of hydroxyl compounds with carboxylic acid derivatives to polyesters (at least one of the starting components containing (meth)acrylate groups) and the reaction of allylidenes, for instance diallylidene pentaerythritol, with alcohols or carboxylic acids. In these reactions, too, the ethylene-type unsaturated vinyl groups remain unchanged and are available as reactive groups for later radical-type polymerisation performed for the purposes of curing.

DESCRIPTION OF THE INVENTION

It has now surprisingly been found that, depending on the preparation conditions, shape and thickness, this polyurethane material when produced according to EP 0 262 488, mostly in the form of lumps reinforced with silylated SiO_2, subsequently to be comminuted to a powder and used as a filler, is more or less flexible, often even elastic, and mechanically mouldable without removal of material. Thus, it has been found amongst other details that this polyurethane material can be produced in the form of film, tape, ribbon, cord, and strand, and also in the form of whatever articles, formed parts or consumer items which within certain limits - depending on the particular chemical composition of the polyurethane matrix and the chosen product shape - can be formed by methods such as bending, twisting, pressing, rolling, and the like. Given the great number of reactive double bonds, and particularly of ethylene-type unsaturated, radical-polymerisable groups present in this material in a chemically bound form as part of the polyurethane matrix, for instance as an acrylic acid or an acrylic acid derivative, a subsequent processing by a combination of mechanical shaping and physicochemical curing is possible.

It is now the task of the present invention to indicate ways to provide this material in a suitable form and produce moulded bodies of any desired shape from it. In fact, contrary to EP 0 262 488, according to the present invention the PU material is not taken as a lump from the reaction vessel after the polyaddition reaction, and then comminuted to powder by grinding, but PU preforms which are more or less flexible, as desired, optionally even plastic, are produced in the non-powder form predetermined and desired for any given application, for instance in the shape of specific formed parts, of consumer items or decorative items intended to be immediately used as such, or in the form of specific three-dimensional structures, preferably as (endless) tape, ribbon, film, strand, profiles etc. to be further processed by mechanical methods, particularly without removal of material, and/or by curing through radical polymerisation.

The term "preform" or "PU preform" is to be understood in the following to cover those products of a specific object form (that is, excluding the form of powder) which consist of the PU material that is present after the completed polyaddition reaction and contains the minimum concentrations of reactive double bonds defined at the outset and present in a chemically bound form that cannot be extracted. The PU preforms can already be used as such for certain applications, or subjected to subsequent shaping, particularly mechanical, with or without removal of material and simultaneous or subsequent radical-induced curing. The resulting final, cured products are summarily designated in the following as "moulded bodies" or "moulded PU bodies" unless the context provides a different interpretation.

It is a task of the invention, therefore, to describe how by twisting, bending, rolling, deep-drawing or similar mechanical actions the reactive polyurethane material can be brought into a desired shape, and is subsequently stabilised and cured in this shape by radical polymerisation via the reactive double bonds.

According to the invention, the reactive unsaturated groups are present as direct, nonextractable chemical components of the polyurethane backbone, but a PU material with similar properties can basically be produced as well by admixing at least some part of these reactive groups in the form of acrylic acid or acrylic acid derivatives to the polyurethane matrix, or occlude them by this matrix. Such an inclusion will for instance occur when the acrylate component is used in an excess over the isocyanate component, and becomes occluded during the non-radical-type polymerisation reaction (polyaddition) by the developing polyurethane matrix. The PU material can also be swelled afterwards by addition of (meth)acrylates, for instance monomethacrylates (MMA).

However, whenever the monomers of the starting mixture are reacted with each other in the stoichiometric ratio, the PU material will be practically free of residual, unreacted monomers, which can be seen from the fact that the double-bond content cannot be reduced by solvent extraction.

By a deliberate choice of the starting monomers, both the flexibility of the preforms and the physical properties, particularly the strengths, of the radical-polymerisation-cured final products can be controlled. The longer the chains of the starting monomers introduced, the more elastic will be the resulting preform, but the lower will on the other hand be the mechanical strength parameters of the definitely cured moulded bodies after radical polymerisation.

It is now the great advantage of the present invention that the PU material present, for instance, in a flat shape such as a film, a tape, or a ribbon, can be used in an extraordinary diversity of ways, and can be brought into the desired shape and definitely cured at the point of use. For instance, in medical practice it can be used to restrain or firmly splint within a few minutes injured limbs by partial or complete enveloping with such a film and subsequent curing by a curing reaction preferably induced by light and particularly by blue light or UV. The half-shells of such splints can also be fashioned directly on the patient. This has the advantage over a traditional plaster cast that eventual pressure spots or other, undesired concomitant symptoms or processes become visible from outside, since the material is transparent, and thus early remedies can be applied. Relative to plastic compositions shaped or cured by heat, the present invention has the great advantage that high temperatures not tolerated by the skin do not arise.

It is a further advantage of the invention that in many applications and particularly in medical or orthopaedic applications of the PU material in immediate proximity to the skin or in direct contact with the skin (such as orthopaedic supports, insoles etc.), only materials can be used which contain no free or extractable monomers so that a potential stickiness of the polyurethane material that otherwise may arise is avoided and that, above all, it is prevented that substances possibly irritating or toxic to the skin are given off or inhaled.

For certain applications where sufficient air permeability of the PU preforms or definitely cured moulded PU bodies must be secured, for instance in replacements for plaster casts or other dressings, the PU material is produced in an air-permeable form,

with processes for air-permeable foaming or subsequent performation of the PU preforms being preferred. Methods for the production of foamed plastics, for instance by the addition of foaming agents or by expansion under decompression, as well as methods for a mechanical perforation of plastics are a known state of the art.

According to the invention, another field of applications of the PU material is the production of articles, elements, and medical aids including bone replacement parts in orthopaedics and orthopaedic surgery as well as the production of dental materials.

Because of the advantageous properties of the definitely cured, moulded PU bodies, particularly with respect to their skin compatibility, attainable hardness, mechanical strengths and/or optical properties, the PU material - simple to use, flexible, and where desired elastic - is also advantageous when used for technical purposes in civil engineering and mechanical design. For instance, pipe connections, ways, borders, sheathing, mounting supports, sound and heat insulations, structural elements, components, casts of objects, moulds, and the like can be produced on the spot with it.

It is a particular advantage amongst others, of the process used according to the invention to produce technical formed parts, relative to traditional processes for the production of these and similar formed parts, that after the first step of production according to the invention, that is, after production of the flexible PU material or PU preform, all low-molecular-weight compounds (monomers) are chemically bound into the polyurethane matrix, and thus are liberated, neither during storage in the form of semifinished product nor during subsequent radical-type curing. Thus, storage, processing and curing occur without emissions and hence can be performed even in locations not equipped with special protective devices such as air-filter installations. The dosing and admixing of special curing agents often practiced in the traditional production for instance of thermoset formed parts also can be dispensed with.

Another essential advantage of the present invention that must be mentioned is the fact that the polyurethane material is also eminently suited for the production of fibre-reinforced composites. To this end it is advantageous to impregnate the fibre materi-

als, particularly loose fibres, nonwoven or woven fabrics of materials such as glass, minerals, carbon or organic polymers, with the liquid starting components prior to the first process step (i.e., prior to the polyaddition reaction), and after that to carry out polyaddition of the reaction mixture containing the impregnated fibre material. In this way a flat, fibre-reinforced polyurethane material can be produced which is not sticky but still flexible enough so that it can be brought into a desired shape and can subsequently be cured to its final strength. By superposition of the flexible, fibre-reinforced polyurethane materials and subsequent thermal and/or photopolymerisation under pressure, composite moulded bodies can be produced in which the layers are chemically bonded amongst each other.

According to the invention, another possibility for the production of fibre-reinforced moulded bodies, particularly multilayer or laminated moulded bodies, from the polyurethane material consists in inserting or incorporating the fibre material only after the polyaddition step between two or more, ordinarily flat blanks or preforms of the polyurethane material, and subsequently polymerising in the heat or under light while applying pressure to generate a definitely cured, fibre-reinforced composite moulded body. During radical polymerisation of the different layers, a homogeneous bonding solidly enclosing the reinforcing fibres develops between the PU preforms. Even complex shapes and components having small or large wall thicknesses can be produced by this method. Such composite moulded bodies can be used wherever traditional composites (fibre composites) can be used, particularly so in motor vehicle and railway construction, shipbuilding, and aircraft construction, but handling of the PU materials or preforms according to the invention is distinctly improved over that of comparable traditional composites (for instance no stickiness, no emission of pollutants).

Another advantage of the present invention that must be mentioned is the fact that the volume decrease or shrinkage occurring during polymerisation reactions of plastics, although it does occur as well in the production processes according to the invention, is substantially less important because of the two-step reaction - first nonradical-type polyaddition, then radical polymerisation - and can be further reduced by the addition

of fillers. For instance, a shrinkage of 3 % and less can be achieved in this way, depending on the composition of the starting components and on filler content, as compared with about 8 % in many traditional plastics polymerisation reactions.

A further advantage of the invention that must be cited is the fact that the PU material and hence also the definitely cured, final product can be adjusted so as to be highly transparent, and in the definitely cured state is very hard and scratch-resistant. The advantages over glass are, amongst others, an improved handling and lower weight of the polyurethane material. Therefore, the PU material, where appropriate fibre-reinforced, is eminently suited also for the production of optical objects such as lenses, headlight glasses, lamp covers, light domes, and covers for solar installations.

Thin films reinforced with endless carbon fibres can further be produced from the PU material, and used as expansion probes. If for instance such a film is glued to a metal beam of a structure, the carbon fibres will tear upon strong elongation of the beam. As the carbon fibres are electroconductive, such an elongation is readily noticed from the resulting circuit interruption, and countermeasures can be initiated before the structure breaks.

By adding powders for instance of aluminium or silver to the PU material, electroconductive films can be produced which can be used in many places, particularly as a protection against electrostatic charge.

According to the invention, mica can be admixed to the starting components and the resulting PU material produced in the shape of insulating tape in order to reinforce the electrical insulating properties of the PU material that anyhow already are present to a large extent. Where required and meaningful, these insulating tapes can also be cured after their stipulated application so that in addition mechanical protection is provided for the insulated part.

Apart from that, the polyurethane material - optionally fibre-reinforced - can of course also be used for the production of everyday utensils, toys, or decorative articles, and

even as a material for sculptors, in which case it is primarily the elastic preforms which can be produced in any desired size and bonded with each other that readily submit to processing without the removal of material (for instance pressing, bending, twisting, etc.) as well as to processing with the removal of material (for instance cutting, milling, carving, grinding, scraping etc.).

For a further increase in mechanical strengths such as flexural strength, tensile strength, and compressive strength, the PU material may contain inorganic and/or nonreactive organic fillers which advantageously are added to the reaction mixture prior to the addition reaction. In this way the physical properties of the PU material can be varied within wide limits. The content of inert fillers in the reactive PU material can be between 0 and 80 % by weight referred to the total weight of the PU material. Contents of 20 to 75 and particularly of 40 to 70 % by weight are favourable for many technical applications.

A large number of inorganic compounds is suitable as fillers. Examples are glass powder, aluminium oxide, silicium dioxide such as quartz, sand or silicic acid, diatomaceous earth, calcium carbonate, clay, talc, pumice, ground slag, mica, asbestos, aluminium sulfate, calcium sulfate, or lithopones. Molybdenum sulfide, graphite, carbon black, fly ash, potassium titanate or fibres such as glass fibres, carbon fibres, or different plastics fibres are also suitable. Glass powder or quartz powder as well as extremely fine silicic acids, particularly microfine fumed, but also precipitated silica are particularly suitable for the attainment of extremely high strengths. Another group of suitable fillers includes representatives such as barium sulfate or rare-earth metal fluorides.

The inorganic filler is preferably superficially silylated in order to facilitate its incorporation into the organic materials and - when using silanes with polymerisable double bonds - to achieve a certain bonding between the organic matrix and the inorganic filler, so that later shrinkage or cracking during the final curing by radical-induced polymerisation can largely be avoided. A particularly preferred silane is

γ-methacryloxypropyl-trimethoxysilane. Other suitable silanes are those with hydroxyl, amino, and epoxide groups.

It is important to take into account when producing the particle or fibre-reinforced PU material that the inorganic filler that might have been added may contain surface groups taking part in the reaction. Thus, silicic acids have silanol surface groups Si-OH that can react with isocyanate groups. Therefore, when adjusting the OH : NCO ratio of the starting components one must account for the amount of such groups present on the inorganic filler.

Suitable inert organic fillers are in particular the acrylic and methacrylic polymers, for instance polymethyl methacrylate, and the polyurethanes. These polymerisates are reduced to the desired particle size by grinding.

The following examples are cited in order to further explain the invention, but shall in no way limit the scope of the invention.

<u>EXAMPLE No. 1</u>

A solution of 47 g bis(methacryloxy-2-hydroxypropyl) sebacate, 32 g tris(6-isocyanatohexyl)biuret and 0.1 g dibutyltin diacetate are placed into a reaction vessel and homogeneously mixed. The mixing may be performed in vacuum in order to avoid the inclusion of air.

The mixture is cast into plate moulds or diverse other moulds, and subjected to the urethane reaction during a time of 60 min at 50 °C. According to DSC, a double-bond content of 1.6 mmole/g of the organic substance is obtained. The resulting elastic plates, films, or moulded bodies can be left as is, or at any later time subjected to further processing for instance by cutting, drilling, rolling, pressing, bending, abrading, milling, etc. and at the same time or right afterwards definitely cured to stable, high-strength moulded bodies by radical polymerisation of the reactive, bound double bonds brought about by heating during 60 min to 100 °C.

EXAMPLE No. 2

In a modification of example No. 1, 51 g bis(methacryloxy-2-hydroxypropyl) adipate, 39 g tris(6-isocyanatohexyl)biuret and 0.1 g dibutyltin diacetate are homogenised. According to DSC, a double-bond share of 1.8 mmole per gramme of organic substance is obtained.

EXAMPLE No. 3

In a modification of example No. 1, 44 g bis(methacryloxy-2-hydroxypropyl) succinate, 36 g tris(6-isocyanatohexyl)biuret and 0.1 g dibutyltin diacetate are homogenised. According to DSC, a double-bond share of 2.0 mmole per gramme of organic substance is obtained.

The following Table 1 provides an overview of the mechanical strengths of the different PU materials produced according to examples No. 1 to No. 3, and hot-cured at a temperature of 120 °C and a pressure of 6 bar:

Table 1

	Starting mixture according to		
	Example No. 1	Example No. 2	Example No. 3
Flexural strength [MPa]	67 ± 4	74 ± 14	86 ± 18
Elastic modulus [MPa]	1753 ± 231	2097 ± 212	2442 ± 80
Surface fibre extension [%]	7.4 ± 1.0	6.23 ± 3.16	6.0 ± 2.8

EXAMPLE No. 4

As a modification of examples No. 1 to 3, 1 % by weight of dibenzoyl peroxide is added to the mixture and the mixture then homogenised. The duration of subsequent radical polymerisation at 120 °C is shortened to 2 - 10 min by addition of the catalyst. Optionally, it is possible owing to the catalyst addition to cure at temperatures far below 100 °C, and particularly at temperatures in the range of 50 to 80 °C.

By pressing, rolling, extruding or deep-drawing, the PU material resulting from the polyaddition is produced in the form of films of different thickness. Several of these films are brought in contact with each other, for instance piled up in layers or glued together with an adhesion promoter (for instance, wetting with acrylate monomer), compressed with pressures of about 2 to 10 bar, and bonded together and definitely cured to composites or laminates by heating to preferably about 100 to 150 °C, and particularly 105 to 120 °C, the individual layers being inseparably bonded together by chemical reactions without forming visible interfaces. By adding coloured pigments to one or several of these films one can generate any desired colour pattern or signal pattern. This process can basically be used with all preforms according to the invention which have not yet definitely been cured by radical polymerisation, so that any desired moulded composite body can be produced.

EXAMPLE No. 5

As a modification of examples No. 1 to 3, 0.3 % by weight of D,L-camphorquinone and 0.5 weight percent of cyanoethylmethylaniline (CEMA) are added to the mixture and the mixture is then homogenised. The homogenised mass is cast into plate moulds, pressed to plates or extruded or deep-drawn to films while adjusting to layer thicknesses of 0.1 to 5 mm. After a reaction time of 60 min at 50 °C the crystal clear, flexible plastic films or plates are withdrawn.

a) From the plates or films having a layer thickness of 0.1 to 1 mm, fingernail shapes are punched out, placed onto the natural fingernails of a test person or glued on with the aid of an adhesion promoter (adhesive), when necessary precisely adjusted to the finger shape with fingernail scissors or other scissors, and cured within 90 s with the aid of a photopolymerisation device having an optical spectrum of 400 - 500 nm. Other objects, for instance orthopaedic insoles, other orthopaedic support elements, decorative articles etc. can be produced in an analogous manner.

b) The film of 1 mm thickness is cut into tapes about 100 mm wide and about 200 to 500 mm long. These tapes are wound around the ends of any two abutting plastic or metal pipes in such a way that they assure two-sided overlap (overlap on the right and left side) of the pipe ends of at least 40 mm, and exactly match or slightly exceed the pipe's contour. The tapes when fixed in this position are then cured within 1 to 10 min by external irradiation with a blue or UV lamp or by simultaneous heating and irradiation with light in a blue light/UV oven. In this way hard, stable gaskets or sleeves are produced, which when using the joint effects of heat and light will in addition yield a water-tight joint at the pipe ends.

c) The film of 5 mm thickness is divided into several parts and treated with textured rollers and presses having different surface patterns. The resulting emboss-ments are fixed in their shapes and definitely cured by simultaneous heating to temperatures of 100 to 120 °C and/or by UV or blue-light irradiation. Decorative or other articles produced in this or similar ways can be further processes by painting, abrading, milling, scratching, etching, etc., both prior to and after the curing.

EXAMPLE No. 6

As a modification of examples No. 1 and 5, 20 % by weight of silylated silica having a mean primary particle size of 40 nm (AEROSIL® OX-50 of Degussa) are added to the mixture and the mixture then homogenised to the largest possible extent.

a) Heat curing (as in example No. 1): the pasty, still flowable mass is then cast into different moulds and subjected to the urethane reaction during 1 h in a heating cabinet at 50 °C. The resulting moulded bodies (in this case simple geometric shapes such as cubes, bricks, balls, tetrahedrons, cylinders, stars, animal figures, and simple testing profiles) are still elastic despite the high filler fraction. These moulded bodies can be left as is if so desired, or at any later time subjected to further treatment for instance by pressing, rolling, bending, abrading, cutting, drilling, milling, scraping, etc. and definitely cured by radical polymerisation, for instance 60 min hot curing at 100 °C, either simultaneously or subsequently, to yield stable, high-strength moulded

bodies. Hot curing can be performed both in a traditional (hot-air) oven or in a microwave device at wavelengths of about 1 to 1000 mm.

b) As an alternative or complement, photocuring can also be performed by irradiation with a UV or blue light source, provided a photocatalyst had been added to the starting mixture, as described in example No. 5.

Of course, both the preforms or moulded bodies produced by nonradical-type polyaddition and the definitely cured moulded bodies can be painted or decorated with paints and varnishes.

EXAMPLE No. 7

As a modification of examples No. 1 - 5, the mixtures specified there are mixed with 5 to 80 % by weightof glass fibres having a length of 0.2 - 2 mm (short staple fibres) and a thickness of 0.1 - 1 mm and further processed as in example No. 1. The fibre-reinforced films, ribbons or moulded bodies produced in different sizes and thicknesses according to this example are distinguished by having a high tensile strength and at the same time elasticity after polyaddition. After radical polymerisation, products having high values of mechanical and physical parameters such as compressive strength, flexural strength, elastic modulus etc. are obtained (see Table 2).

Table 2: Comparison of reinforced moulded bodies after definite curing by radical polymerisation at 120 °C and 6 bar; **starting mixture of the reaction components as in example No. 1**

	Flexural strength [MPa]	**Elastic modulus [MPa]**	**Surface fibre extension [%]**
5 wt.% short-staple glass fibres, not silylated	108.3 ± 14,3	2818 ± 491	4.41 ± 0.42
Glass fabric soaked with Ex. No. 1 start. mixture	266 ± 36	18669 ± 2434	3.59 ± 0.24

Moreover, when glass fibres and other fillers are incorporated, the shrinkage due to polymerisation which anyhow is already slight (for instance about 3 % in examples No. 1 to 5) decreases to a fraction of this value.

EXAMPLE No. 8

In a modification of example No. 5, the given mixture is mixed together with 20 % by weight of AEROSIL® OX-50 of Degussa, and heated to 50 °C and homogenised in a screw extruder. Instead of camphorquinone and CEMA, 0.5 weight percent of 2,4,6-trimethylenebenzoyldiphenylphosphinoxide are added as a photocatalyst.

At low pressure the mass is conveyed to an endless tape through a flat sheet die having an opening of 5 mm in height, then optionally rolled out to a thickness of 1 - 1.5 mm, and finally subjected over a period of 1 to 2 h at a temperature of 50 °C to the urethane reaction in a zone for further processing. The share of double bonds in the resulting fibre-reinforced PU plates, tapes or films and tissue is 1.6 to 2.0 mmole per gramme of the organic substance.

The fibre-reinforced films, tape, or ribbons produced according to this example in different sizes and thicknesses are distinguished by high elasticity. They can be brought into different fanciful-decorative or useful shapes by torsion, twisting and/or bending, and then cured within 1 to 5 min by irradiation with wavelengths of 300 to 500 nm, for instance in a photodevice having a light intensity of 18,000 lux. The curing can be accelerated or improved to a significant degree by simultaneous or subsequent heating to about 50 to 120 °C. The resulting objects are distinguished by high shock resistance and fracture resistance.

EXAMPLE No. 9

In a modification of examples No. 1 to 5, a glass fabric is impregnated with the homogenised mixtures, and pressed to a thin layer. After polyaddition a nonsticky, readily mouldable impregnated tissue is obtained. High-strength moulded bodies or

plates which for instance can be used as printed circuit boards in the electronics industry are obtained by piling up two or more layers of this tissue, optionally after wetting with short-chain acrylate or methacrylate monomer, and subsequent radical-type thermal and/or photopolymerisation under pressure. Where extremely high strengths are desired, silylated glass fibres can be used in particular.

By using unidirectional fibre strands rather than nonwoven or woven fibre fabric, and staggered superposition of the resulting impregnated layers, the composite or laminate can be optimised specifically with respect to the desired force vectors.

EXAMPLE No. 10

Comparison of the curing times for different curing methods of the polyurethane material:

a) Without catalyst addition, radical polymerisation of the preforms should preferably be performed at temperatures of about 100 to 150 °C. Here the reaction time is 10 (at 150 °C) to 60 min (at 100 °C).

b) Heat curing of acrylate and methacrylate polyurethanes with suitable catalysts added:

Table 3

Catalyst added	Temperature		
	80 °C	100 °C	120 °C
Dibenzoyl peroxide	60 - 120 min	5 - 15 min	2 - 10 min
tert-Butyl peroctoate	30 - 100 min	5 - 10 min	1 - 3 min
Benzopinacol	24 - 72 h	1 - 5 h	3 - 10 min

c) Photocuring of acrylate and methacrylate polyurethanes with suitable catalysts added:

Table 4

Light intensity: Spectrum:	450 mW/cm^2 400 - 500 nm	18,000 lux 400 - 500 nm	18,000 lux 300 - 500 nm
Camphorquinone	20 - 120 s	4 - 10 min	3 - 5 min
2,4,6-Trimethylenebenzoyl-diphenylphosphinoxide	n.d.	2 - 15 min	1 - 5 min
Benzil dimethyl ketal (Irgacure® 651)	n.d.	n.d.	3 - 10 min

n.d. = not determined

Definite curing with the aid of light strongly depends on the layer thickness of the polyurethane material, the coloration, and where applicable the amount of fibre materials and/or fillers present. Photocuring can be accelerated or improved with respect to the depth of curing and to surface hardness by amine additions (for instance triethanolamine).

The hardness or physical strength of the moulded bodies can once more be raised to a significant degree by a simultaneous or subsequent heat treatment at temperatures of about 100 - 120 °C lasting 5 - 10 min.

Both for photocuring and for hot curing, catalysts commonly are added in amounts of up to 5 % by weight, and particularly of about 0.1 to 1 % by weight. In the present example the catalyst content in cases (b) and (c) is close to 1 % by weight.

EXAMPLE No. 11

A rope of PU material 10 m long and with a diameter of 1 cm, made according to example No. 5, is helically twisted and brought to an approximate S-shape. The thus shaped preform is cured over a period of 10 min by photopolymerisation. One end of the crystal clear moulded body is then brought in direct contact with an incandescent lamp or halogen lamp that is darkened in all directions; this combination is placed into a dark room. When switching on the lamp the light of which cannot directly illuminate the room, the light is transported through the moulded PU body and distributed in the room. In similar fashion different PU materials and the moulded bodies that can

be produced from them can be used to achieve fanciful luminous effects and decorative lighting.

EXAMPLE No. 12

For the production of particularly decorative moulded bodies, coloured pigments, for instance inorganic oxides such as iron oxide or titanium dioxide can be added prior to the polyaddition reaction to the original component mixture in concentrations of preferably between 0.1 and 5 % by weight.

PATENT CLAIMS

(Demand filed on 24th Octobre 2000)

1. Method for the production of moulded bodies on the basis of a polyurethane material where

a) a preferably flowable mixture of starting components is prepared which contains, on one hand isocyanate and on the other hand monomers with reactive double bonds and containing hydroxyl groups, preferably acrylate or methacrylate containing hydroxyl groups, where the monomers containing hydroxyl groups are used in a stoichiometric ratio or in less than the stoichiometric amount relative to isocyanate; and

b) the mixture is subjected to a nonradical-triggered polyaddition reaction generating a radical-polymerisable preform having a contant of nonextractable, reactive double bonds - that can be determined by DSC - of at least 0.5 mmole/g and is free of extractable monomers with reactive double bonds;

characterised in that the mixture before or during the polyaddition reaction is brought to a desired form by methods of plastics engineering known per se, in particular by casting, pressing, rolling or extruding, and the resulting flexible, where applicable elastic preform is definitely cured to a structurally rigid moulded body at any time, preferably after a further forming, particularly without the removal of material, by radical-triggered polymerisation of the reactive double bonds.

2. Method according to claim 1, characterised in that the mixture of starting components contains isocyanate and (meth)acrylate containing hydroxyl groups in a ratio of about 1 : 1 between the OH and NCO groups, and that at least one of the starting components is at least bifunctional, preferably tri or polyfunctional.

3. Method according to one of the claims 1 or 2, characterised in that the curing by radical-triggered polymerisation occurs essentially without emissions.

4. Method according to one of the claims 1 to 3, characterised in that the preform is produced in the shape of a film, tape, ribbon or any mould, and subsequently sub-

jected to at least one further forming, preferably without the removal of material, for instance by bending, twisting, pressing, rolling, or deep-drawing.

5. Method according to one of the claims 1 to 4, characterised in that to the starting components at least one of the following components is added: a filler, a fibre material, a coloured pigment.

6. Method according to one of the claims 1 to 5, characterised in that a definite curing of the preform occurs by radical polymerisation of the free double bonds while applying elevated pressure and/or elevated temperature and/or irradiation with microwaves or energy-rich radiation, particularly ionising radiation.

7. Method according to one of the claims 1 to 6, characterised in that to the mixture of starting components at least one catalyst adapted to trigger and/or accelerate a radical-type polymerisation of the reactive double bonds is added, particularly a hot-curing or photocatalyst, in an amount of up to 5 % by weight, preferably 0.1 to 1 % by weight.

8. Method according to one of the claims 1 to 7, characterised in that two or more preforms, particularly in the form of films, tapes, ribbons, or plates, which are brought in mutual contact, preferably piled up as layers or glued together with the aid of an adhesion promoter, are bonded together while applying elevated pressure and elevated temperature to yield composites or laminates of any desired layer thickness, and definitely cured, where appropriate with the aid of light.

9. Method according to claim 8, characterised in that fibre material, particularly in the form of woven or nonwoven fibre fabric, is inserted between the preforms prior to definite curing by radical polymerisation.

10. Method according to one of the claims 5 to 9, characterised in that to the starting components a filler is added in a concentration of at most 80 % by weight, preferably of 20 to 75 and particularly of about 40 to 70 % by weight.

11. Method according to one of the claims 5 to 8, characterised in that the fibre material is present in the form of unidirectional fibre strands, woven or nonwoven fibre fabric and preferably contains glass fibres, carbon fibres, aramide fibres, polyethylene fibres, cellulose fibres, and/or other suitable plastic fibres.

12. Method according to claim 11, characterised in that the fibre material prior to the polyaddition reaction is impregnated with a mixture of the starting components, and then moulded in the form of plates or film and subjected to the polyaddition reaction.

13. Method according to claim 6, characterised in that the curing of the preform occurs at a pressure of 2 to 10 bar and/or a temperature of 80 to 150 °C and/or under irradition with light having a wavelength of 300 to 500 nm or with microwaves having a wavelength of 1 to 1000 mm.

14. Moulded body on the basis of a preform produced by a nonradical-triggered polyaddition reaction, with a polyurethane matrix from isocyanate and monomers with reactive double bonds containing hydroxyl groups, particularly (meth)acrylate containing hydroxyl groups and, where appropriate, from further additives, where the monomers containing hydroxyl groups are present in a stoichiometric or substoichiometric ratio relative to the isocyanate and the preform has a content of nonextractable, reactive double bonds - that can be determined by DSC - of at least 0.5 mmole/g and is free of extractable monomers with reactive double bonds, characterised in that the preform is present in the form of a structurally rigid object or formed part definitely cured by radical polymerisation of the reactive double bonds.

15. Moulded body according to claim 14, characterised in that prior to the polyaddition reaction, isocyanate and (meth)acrylate containing hydroxyl groups are present as the starting components in a ratio of about 1 : 1 of the OH and NCO groups, and that at least one of the starting compounds is at least bifunctional, preferably tri or polyfunctional.

16. Moulded body according to one of the claims 14 to 15, characterised in that it is colourless and translucent, more particularly crystal clear.

17. Moulded body according to one of the claims 14 to 16, characterised in that it contains at least one of the following additives: filler, fibre material, coloured pigment, and/or exhibits a surface treatment, particularly a coating, coloration, painting and/or texture.

18. Moulded body according to one of the claims 14 to 17, characterised in that it is present as a cured composite or laminate formed from at least two curable preforms.

19. Polyurethane-based moulded body that can be obtained by a method according to one of the claims 1 to 13.

20. Use of a flexible, where appropriate elastic preform with a polyurethane matrix produced by a nonradical-triggered polyaddition reaction from isocyanate and monomers with reactive double bonds containing hydroxyl groups, particularly (meth)acrylate containing hydroxyl groups, and where appropriate further additives, which has a content of nonextractable, reactive double bonds - that can be determined by DSC - of at least 0.5 mmole/g and is free of extractable monomers with reactive double bonds, for the production of a structurally rigid object or formed part by definite curing of the preform via radical polymerisation, preferably free of emissions, after or during a further mechanical forming of the preform, particularly without the removal of material.

21. Use according to claim 20, where the further processing and simultaneous or subsequent definite curing of the preform occur directly at the point of use.

22. Use according to claim 20 or 21 for the production of technical formed parts, design and support elements, optical wave guides, tool components, covers and

protective films, electrical, thermal or acoustic insulating elements, toys, utensils, art objects, or decorative objects.

23. Use of a moulded body according to one of the claims 14 to 19 for the production of technical formed parts, design and support elements, optical wave guides, tool components, covers and protective films, electrical, thermal or acoustic insulating elements, toys, utensils, art objects, or decorative objects.

24. Use according to one of the claims 20 to 23, for applications in medicine, dentistry, civil and mechanical engineering, fastening technology, insulating and packaging technology, the automotive industry, measuring technology, households, as well as in fine art.

UNITED STATES OF AMERICA COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION	OFGS FILE NO. P/167-

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural inventors are named) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

MOULDED BODIES MADE FROM A POLYURETHANE MATERIAL, PRODUCTION AND USE THEREOF

the specification of which is attached hereto, unless the following box is checked:

☒ was filed on 15 October 1998 as United States patent Application Number or PCT-International patent application number PCT/EP98/06558 and was amended on 3 November 2000 (if any).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information known to be material to patentability in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim priority benefits under Title 35, United States Code §119 of any foreign application(s) for patent or inventor's certificate or United States provisional application(s) listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign or Provisional Application(s)

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. 119
			YES _X_ NO ___
			YES ___ NO ___

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

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